5-13-1977

Image Intensification by Superimposed Vesicular Images Generated by Decomposition of Hydrogen Peroxide

William Grabenstetter

Image Intensification By Superimposed Vesicular Images Generated By Decomposition of Hydrogen Peroxide

By
William R. Grabenstetter

Submitted to the Rochester Institute of Technology,
Department of Photographic Science and Instrumentation
May 13, 1977
Advisor: Dr. R. Francis

Abstract

In the late 1960's, Weyde discovered that treating conventionally processed silver halide films with hydrogen peroxide led to intensified densities by the superimposition of vesicles at the silver image sites. This project attempted to reproduce the results of 5°- 10°DIN speed increase and excellent sharpness mentioned in the patents issued to Weyde. Using the patents as a reference, a paste of urea hydrogen peroxide and PEG was examined as an image intensifier, with no success. Alternate binders suggested in the patents were then examined, Triton X-405 proving to be the best. A paste of 4g. urea hydrogen peroxide in 10 ml. Triton X-405 produced strips of from zero to two stops increase in speed and gamma as high as twenty-five on Copex Pan, (a slow speed microfilm). The excellent definition quoted in the patents was never realized.

Introduction

In the late 1960's, Edith Weyde was experimenting with gases which destroy silver images. In the process, she discovered that by treating silver halide emulsions with hydrogen peroxide, an increase in density could be achieved. She discovered that the hydrogen peroxide reacted at the silver image sites and was catalytically decomposed, releasing oxygen, which formed bubbles upon heating. These bubbles, or vesicles, at or near the image silver, diffracted transmitted light and resulted in increased density. The silver image absorption plus the diffraction of the superimposed bubble led to a density higher than the silver image absorption alone.

In October 1971, she patented[1] the process which describes the treatment of conventionally processed film with hydrogen peroxide by subjecting the film to a solution or a vapor of hydrogen peroxide, followed by heating, which expanded the bubbles to about 1 μm in diameter. A speed increase of 8°DIN (about 3 stops) was quoted when a film rated at 15°DIN was exposed as if it were rated at 25°DIN and subsequently treated by the process. Excellent sharpness was also quoted, and applications to microfilm were suggested.

In October 1973, Weyde was issued a patent[2] claiming that speed increases of 5°-10°DIN may be obtained by "over-rating" the film, processing, coating it with a paste of carbamide perhydrate (an addition compound of hydrogen peroxide and urea), and heating. The heating causes the carbamide to decompose and release hydrogen peroxide, which then reacts with the silver as mentioned above. The advantage of using a paste developer is greater control over the amount of hydrogen peroxide present For this reason, the paste method was examined, the vapor and

solution methods having already been examined.[3]

At the Third International Congress on Reprography, in London in March 1971, Weyde et al. delivered a paper on the process. The paper describes specific emulsions, a percarbamide paste, and various heating methods. H & D curves were given, showing "before and after" comparisons of the image intensification process. From the paper, we are led to believe that by subsequent heating of the treated film with water vapor of 50°- 70°C., an increase in both speed and contrast is obtained. Heating by infrared radiation or a hot roller results in an increase in contrast and a very substantial increase in speed. Using a flash of high-intensity radiation to heat the film results in an increase in contrast only. Once again, excellent sharpness was claimed.

The obvious advantages of the process are that less silver is needed to produce a given gamma and Dmax with the process than without it, and that speed and contrast of existing films may be "pushed" without loss of definition.[1] The disadvantage is that the process does not seem to lend itself to duplication. Lewis of Indiana State University wrote a paper describing hydrogen peroxide treatments resulting in an ASA of 3200 for Tri-X film.[4] The results could not be reproduced.

Staub and Woo[3] experimented with the process in 1975 at RIT, with little success. Their work dealt with examining the vapor and solution methods of introducing the hydrogen peroxide, and various methods of subsequent heating. Vesicular images superimposed on the silver images were obtained; however, speed losses resulted, and sharpness was very poor.

Experimental

Note: Many avenues were examined in the course of experimentation, most without success. For this reason, many intermediate results are listed in this section to show the logical progression of the experiment.

It seems reasonable that to reproduce results quoted in the literature, one should reproduce the methods in the literature. This project tried to follow specific examples in the literature as closely as possible. A specific film mentioned in the literature is Copex Pan. Copex Pan is a slow speed microfilm quoted as having about 0.2 grams of silver per square meter.[5] The literature also describes a paste which is to be applied to such a film. Briefly, the recipe quoted for image intensification is:

1) Expose the film to form an image.
2) Develop in the following:

H_2Q	3g
p-methyl-aminophenol	1g
sodium sulfite	40g
sodium carbonate	26g
H_2O	to 1l.

3) Fix in sodium thiosulfate solution, wash and dry.
4) Coat the film to a thickness of 0.2 - 3 μm with a paste consisting of:
   15g percarbamide
   85g ethylene glycol (mol. wt. 6000 - 12,000)
5) Heat for 30 seconds at 90°C.

The first task was to follow the above procedure. A device was obtained for coating the paste onto the film. It consisted of a handle and a stainless steel rod wrapped tightly with stainless steel wire. Coatings were made by placing a "puddle" of the coating substance between the rod and the area to be coated. The rod was pulled across the area to be coated, the

substance was spread out and escaped onto the base, or area to be coated, through the gaps in the wire on the rod.

It was proposed that a factorial experiment be run, the factors being percarbamide concentration, temperature of heating, and duration of heating. Each factor was examined at three levels, temperature, 85°, 90°, 95°C; time, 20, 30, 40 seconds; percarbamide concentration, 13, 15, 17 grams. The response variables were speed and gamma. Speed is defined as log H values to give 0.1 over base plus fog, as read on the Quanta Scan Automatic Recording Densitometer, with matched f/4.5 optics[6].

An ample number of test strips for a 3x3 factorial were processed in the developer described, using nitrogen burst agitation. Processing times were: developer, 2 minutes; stop, 30 seconds; fix, 2 minutes. The film was exposed in a Kodak 101 sensitometer, standard exposure, with a 2.4 neutral density filter. This resulted in strips underexposed by three stops relative to strips exhibiting a full density range (clear to dark on a 0 - 3.0 continuous wedge). Nitrogen agitation was set up such that the developer and fix recceived 0.6 seconds agitiation every ten seconds. At this point, work was held up for about three weeks while waiting for the urea hydrogen peroxide to arrive.

Once the compound arrived, the first project was to make practice coatings. A small batch of paste was made by heating 5 grams of the urea hydrogen peroxide compound and 28.35g of the polyethylene glycol (mol. wt. approx. 6000). The dry mixture was heated at 53°C for ten minutes, at which time the temperature was increased to 60°C to obtain a less viscous paste. The paste was white in color and had the consistancy of thick "Cream of Rice." A coating was made on a processed sensi-strip which was secured to a coating block by double-stick tape. The coating block was used to keep the film warm by running warm water through the block, so that the

wax would not coagulate upon coating. The paste was too thick to coat evenly.

It was then learned upon close re-examination of the patents that the process for making the paste was incorrect. A second paste was made. 28.35g of polyethylene glycol was melted at about 75°C and cooled to about 60°C. The urea hydrogen peroxide was then added and ground to a uniform consistency in a heated mortar and pestle (so wax wouldn't coagulate). A coating was made and the strip was placed in the oven to see what sort of results might be expected. The oven temperature was 90°C and the strip was left for thirty seconds as per patent instruction. Results: no effect could be determined because as soon as the strip was removed the wax would cool and coagulate, making it nearly impossible to see any detail in the strip whatsoever. The strip was cooled and bent in an attempt to peel off the wax. This was, for the most part, unsuccessful. Several more coatings were made and placed in the oven at 110°C for times up to five minutes with similar results.

At this point it became clear that the project could not continue along the scheduled guidelines. There was no sense in running a factorial experiment that doesn't produce any usable results. Before further work could continue, an image-wise vesicular image had to be produced.

There was some concern as to whether or not the decompostion point had been reached. A melting point apparatus, in conjunction with potassium iode test paper, was used to determine the decomposition temperature. The test paper was held near the percarbamide to be tested (it turns blue upon exposure to hydrogen peroxide). The apparatus was set to increase approximately 1°C per minute. After several attempts, the decomposition point was determined to be between 70° and 75°C. This indicates that the oven temperature was correct for the

percarbamide compound chosen.

The next project was to find a solvent to remove the wax from the strips and see if vesicles had been formed but were not visible due to the wax coating. The solvents tried were: benzene, ethyl alcohol, and a petroleum ether.[7] None were solvents for the ploye thylene glycol.

The next project was too see if, in fact, the percarbamide would produce vesicles of any sort. Strips were taped on the inside of a beaker. Some of the percarbamide compound was placed in the bottom and heated. Upon decomposition, some of the compound turned to ash and settled upon the strips; the compound fumed and sputtered, melted, and a strong ammonia odor was present. Examination of the strips showed a white "frost" on the strips close to the bottom of the beaker. The frost was thought to be the ash that had settled upon the strips. Indeed, some of it was. The area closest to the compound, however, showed indications of vesiculation; the area looked dark in transmitted light. The vesicles were not image-wise, however. More experiments were run to see if an image-wise superimposed vesicular image could be obtained. Strips were "fumed" in the steam rising from boiling water at pH of approximately 10, and then fumed over a beaker where the percarbamide was heated and decomposing.

The strips showed no overall vesiculation. They do, however, exhibit some small "frost" spots which were suspected to be blisters from vesiculation; these also are not image-wise.

Several films were tested to see if vesiculation would occur using the solution method of hydrogen peroxide induction described by Staub and Woo[3]:

> "...immerse the strip for five seconds in a 30%

hydrogen peroxide solution, squeegee, and heat in a vapor of boiling water at pH 12 to expand bubbles."

Once successful vesiculation had been obtained, that film would be examined with the paste. A strip of Copex film was immersed in a beaker of 30% hydrogen peroxide for five seconds. Immediately upon immersion, bubbles streamed from the high density end of the strip; it was assumed that this was oxygen escaping from the emulsion as the hydrogen peroxide decomposed at the silver sites. The strip was then squeegeed and heated for about ten seconds as described above.

The silver in the high density end of the strip had been dissolved. Several trials were run at lesser times to see if less exposure to the hydrogen peroxide would stop the destruction of the silver in the strip. A time of three seconds seemed to be best; the strip showed a visual increase in density toward the low density end. When scanned, the strips showed a "hump" in the H & D curve. (For graph, see Appendix, Fig. 1)

The "hump" seems to show that silver concentration which is best suited to the process. The silver concentration at that point is such that the hydrogen peroxide can decompose at the image sites and form oxygen bubbles that provide greater diffraction density than the silver absorption density, so there is an increase in density. Beyond the hump, the greater concentration of silver is the dominating element in the density, providing more absorption than the process does with diffraction. Speed values (defined as log H values to give 0.1 over base plus fog density; the lower the number given, the greater the speed) were 1.6 - 2.1. Gamma values (slope of the straight line portion of the curve) were in the neighborhood of 4.0 before the hump and 8.0 after the hump. Control values were speed, 2.2, and gamma, 3.5. In other words, the process resulted

in both a speed and contrast increase. It was now assumed that if Copex film could produce vesiculation with the solution method, it should produce vesicles with the paste method. No other films were examined, as the Copex film did produce vesicles and, as previously mentioned, it was the aim of this project to follow the literature as closely as possible. Copex was mentioned in the literature.

There was concern that perhaps the choice of the urea hydrogen peroxide from P & B Chemicals was incorrect for some reason.[8] In this light, the percarbamide compound (1:1 mole ratio of urea and hydrogen peroxide) was to be synthesized as indicated below:

60.06 grams urea
34.02 grams hydrogen peroxide (113.4 ml 30% hydrogen peroxide)

The urea and hydrogen peroxide were combined in a beaker. The resultant slurry had to be dried somehow. It could not be boiled, as this would cause the compound to decompose. A vacuum evaporation apparatus was obtained from the chemistry laboratory and used to dry out the mixture for use. The process of drying took about one week, all the while maintaining a vacuum using a Richards pump and having the beaker surrounded by ordinary desiccator chips in the plastic sphere of the apparatus. When the compound had dried, an accident in the laboratory caused it to become contaminated. It had to be remade. This time, phosphorus pentoxide was used as a desiccator. The drying time was now four days.

The percarbamide synthesized in the laboratory was tested by placing some in the bottom of a beaker and heating, steaming a strip in the vapor of boiling water (pH 10), and fuming the strip in the vapor rising from the decomposing percarbamide. Vesiculation did occur, mostly image-wise. It appeared to be most like what the patents described. The tested strips

were scanned and showed a slight gain in speed and contrast over the controls. Some showed a speed decrease as the peroxide "ate up" the silver at the low density end. It was thought that the synthesized compound was better than what was provided by P & B Chemicals because it produced vesiculation. A paste was made using 28.35 grams polyethylene glycol and 5 grams of the synthesized percarbamide, as described previously. A strip was coated and heated. No vesiculation could be seen through the wax. An unsuccessful attempt was made to wipe the molten wax from the strip. An experiment was run to see how well the hydrogen peroxide was released from the molten polyethylene glycol. A paste mixture was made and heated, and a potassium iodide starch test strip was bathed in the vapors. It did not turn blue, indicating no, or very little, hydrogen peroxide was being released. For some reason, the wax seemed to inhibit the release of the hydrogen peroxide.

Enough time had passed such that the synthesized percarbamide had decomposed and another batch had to be made. The compound was tested. A small amount was placed in a beaker and heated. The fumes turned the test paper blue, indicating that it was releasing hydrogen peroxide. The same compound was then placed in some of the polyethylene glycol wax and heated. Again, the wax seemed to inhibit the release of hydrogen peroxide. Two experiments had shown the same results. A different binder had to be found. Several compounds were mentioned in the patents as lowering the melting point of the polyethylene glycol or could be used alone for the process. They are: other polyethylene glycols, low aliphatic alcohols, polyglycol ethers, alkyl polyglycol ethers, fatty alcohols, methylene glycols, organo polysiloxenes, and fatty acids. The following compounds were examined, being easily available from the chemistry laboratory stockroom: glycerol, diethylene glycol, Triton X-405 (an alkyl polyether alcohol). Pastes were made from the above in conjunction with polyethylene glycol to lower its melting point, and from the above compounds alone.

Triton X-405 alone proved to be the best. About 10 ml of the substance was put in a beaker and a measure of the percarbamide was added and mixed. The mixture became creamy white and frothy. A strip was steamed, coated, and heated in the oven at 90°C for thirty seconds and the paste was wiped off. Vesiculation had occured, mostly image-wise; however, some was present in streaks in the non-image area, possibly due to non-uniform coating. The percarbamide provided by P & B Chemicals was examined in the same paste with similar results. This compound was used in all other pastes as there was more of it, and it was easier to buy than to make. The key to the process seemed to be steaming, to soften the emulsion, and the use of Triton X as a binder.

The process was applied to some underexposed negatives lying about the laboratory (Plus-X and Tri-X). They showed little detail and it was impossible to determine what the scene was in some frames. After the treatment, the scene proved to be of a football game.

A attempt to increase the coated paste thickness was made by using a large gauge wire coating bar. This proved to be worse than the medium gauge roller. It resulted in a lot of streaking in the coating. A narrow gauge roller and a knife-edge were tried, but these resulted in too thin a coating to provide enough hydrogen peroxide for vesiculation.

The factorials described could now be run, since a process that will produce vesicular images from a paste of percarbamide had been found. The levels were revised, due to a better knowledge of the process. The levels were: Temperature, 80°, 90°, 100°C (actually, 80°, 93°, and 104°C, due to problems in adjusting the oven temperature); time, 15, 30, 60 seconds; percarbamide concentration, 1, 2.5, 4 grams per 10 ml Triton X-405.

Results from the first factorial showed that the greatest increase is seen in contrast. Speed also tends to increase about one stop with increasing temperature and concentration. The curves exhibited the same general shape as those treated with the hydrogen peroxide solution and were quite noisy. It was sometimes very difficult to determine the response values due to the excessive noise in the traces. The noise was thought to be caused by at least two factors: the method of coating, and the method of removing the paste. (See Appendix, Fig. 2 and Fig. 3)

Coating had been accomplished by using a coating roller - a bar or rod with coiled wire on it. This tended to produce streaks in the strip corresponding to the spacing between the wires. The paste was removed by wiping the strip with a paper towel; this was a messy process and often required moderate pressure, which may have acted to squeeze out the bubbles in the emulsion. A new coating system was suggested. Since the coating knife alone did not provide a thick enough coating, the strip was bracketed on both sides by three pieces of film held together and onto the coating block with double stick tape. The paste was then applied in the trough and leveled off with the coating knife. This gave visibly uniform coatings. (See Appendix, Fig. 2 and Fig. 4)

A cold water spray was examined as a method of removing the water-soluble paste, hoping that the cold water would not soften the gel and release the vesicles - which it did. Film cleaner was then tried and seemed to work well, although quite a lot was needed to remove the paste entirely.

While coating some strips, a few were inadvertently not steamed prior to coating, as had previously been thought correct. These strips showed less noise, with an equal increase in contrast. A series of strips were run with no steam treatment.

These also showed speed as well as contrast to be proportional to concentration and temperature. An average process error of 11.11% was found in these coatings. The process also seems very susceptible to handling. Scratches in the emulsion split open under the pressure of vesiculation. Severe and even moderate bending of the strip while coated with the paste led to streaks of high density areas. A set of strips were scanned with matched f/5.6 optics to see if an increase in contrast would result. A slight increase was realized, and the base plus fog level was increased. The contrasts are very high to begin with, so using more specular optics doesn't have much of an effect.

Some scenes were photographed on Plus-X Pan film, and processed in D-76 1:1 at 68°F as per instructions. These consisted of a series of scenes: one at normal exposure, one at -3 stops, and -5 stops. The underexposed scenes were then treated with the paste to see if they could be successfully printed. Both the -3 and -5 stop shots could be printed acceptably, but both had an equal loss of definition. The prints appear rather like x-ray images in that they are blurry and "out of focus." Those scenes underexposed by 5 stops and not treated with the paste had very low contrast, and, while sharper, seemed to contain less information about the scene as a whole. (See Appendix, pages 18 - 20)

Summarized Results

*The process does not give a substantial increase in speed.
*Contrast is greatly increased.
*The process is very susceptible to handling.
*Detail is lost in the intensified image.
*High Dmax is achieved, usually above 4.0 (machine maximum).
*There is a large error in the process.
*The process produces visually recognizable images of scenes that are 4, 5, and even 7 stops underexposed.

Conclusions

The results seem to correspond to those of Staub and Woo. Only a moderate speed increase is found, while gamma is increased greatly. The entire process seems to be a delicate balancing act of dosing the correct amount of hydrogen peroxide to produce vesiculation. Too little, and no effect is seen; too much, and the silver image is destroyed. Future work may involve a "fine-tuning" experiment to find the correct level of peroxide for a given film. The range chosen for this experiment was too large. Another choice of binders might also be advantageous.

As seen, the process does produce prints of acceptable contrast from negatives underexposed by as much as 5 stops and perhaps more; yet, the "excellent definition" described in the patents was not realized. Again, corresponding to the results of previous work done at RIT. The process, due to its high error, does not seem to be commercially applicable. One could not accurately predict the outcome of a treated negative.

On the whole, the process seems to be at the "curiosity" stage. Perhaps further experimentation can make it a practical image intensifying system one day. It is the opinion of the author, however, that that day is far distant.

Appendix

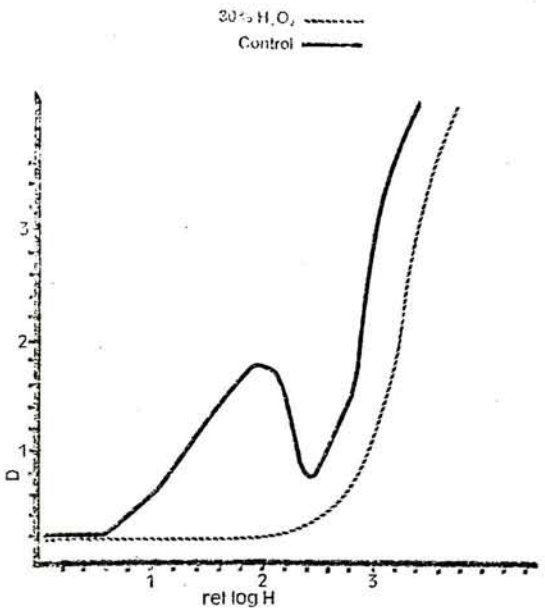


Fig. 1

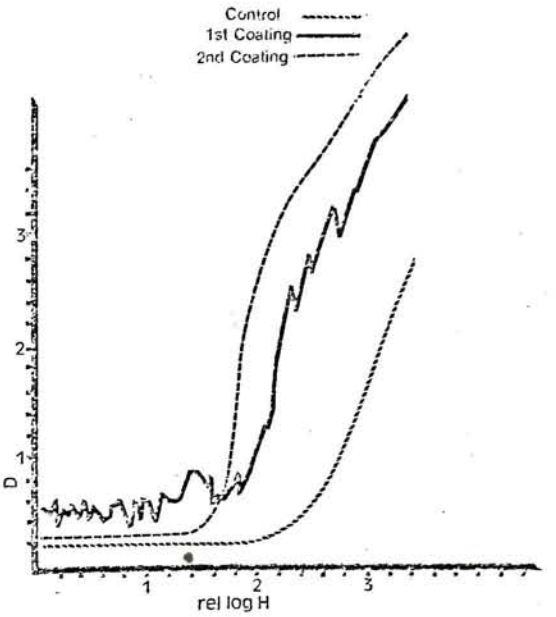


Fig. 2

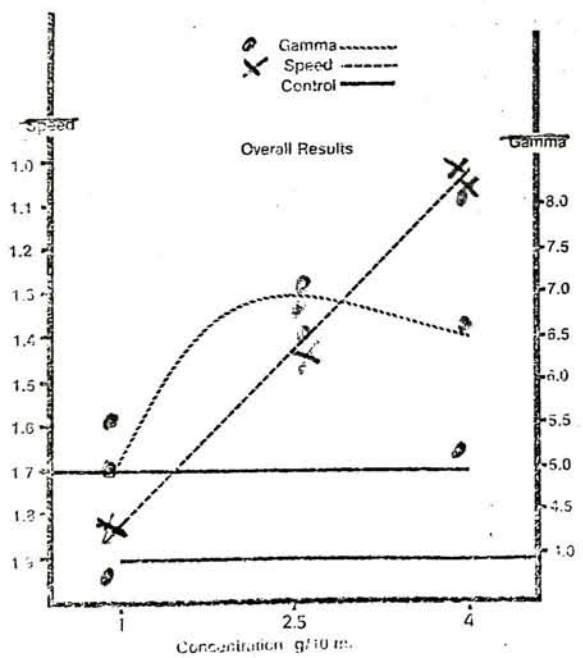


Fig. 3

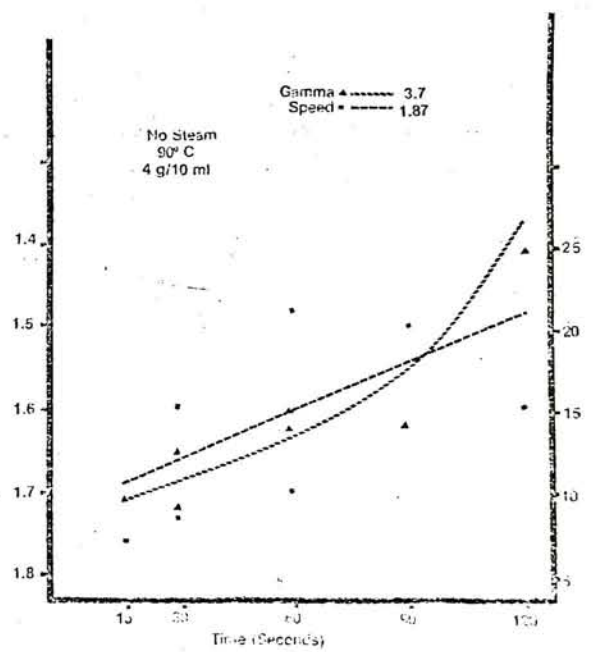
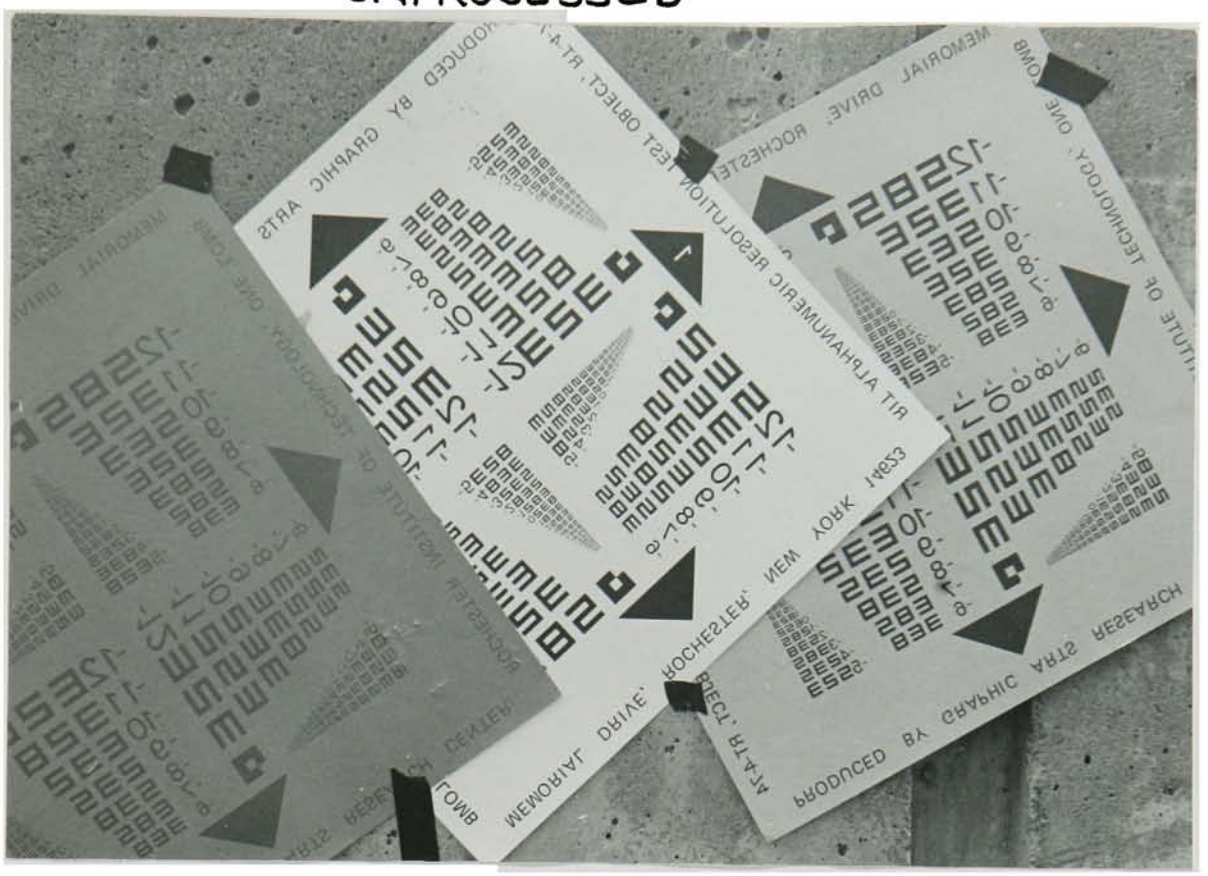
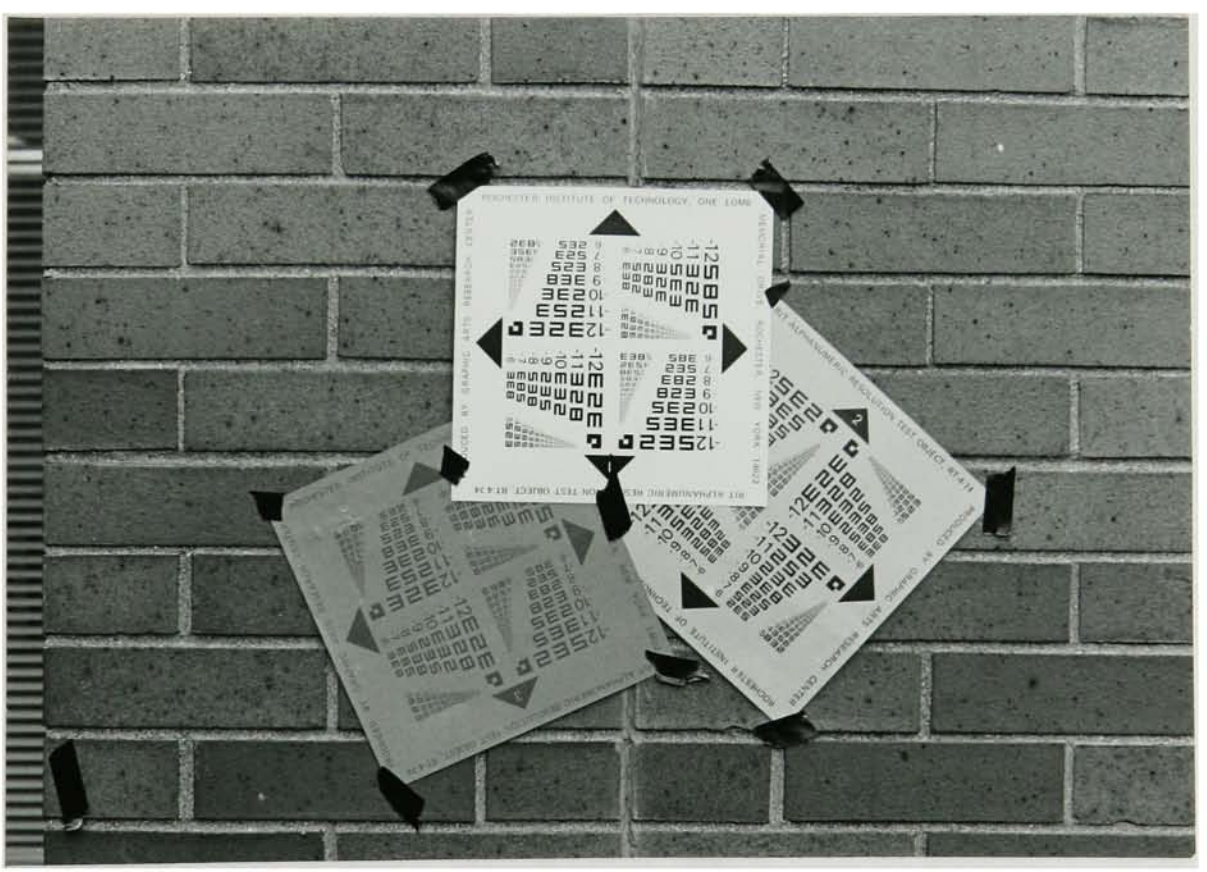


Fig. 4

UNPROCESSED

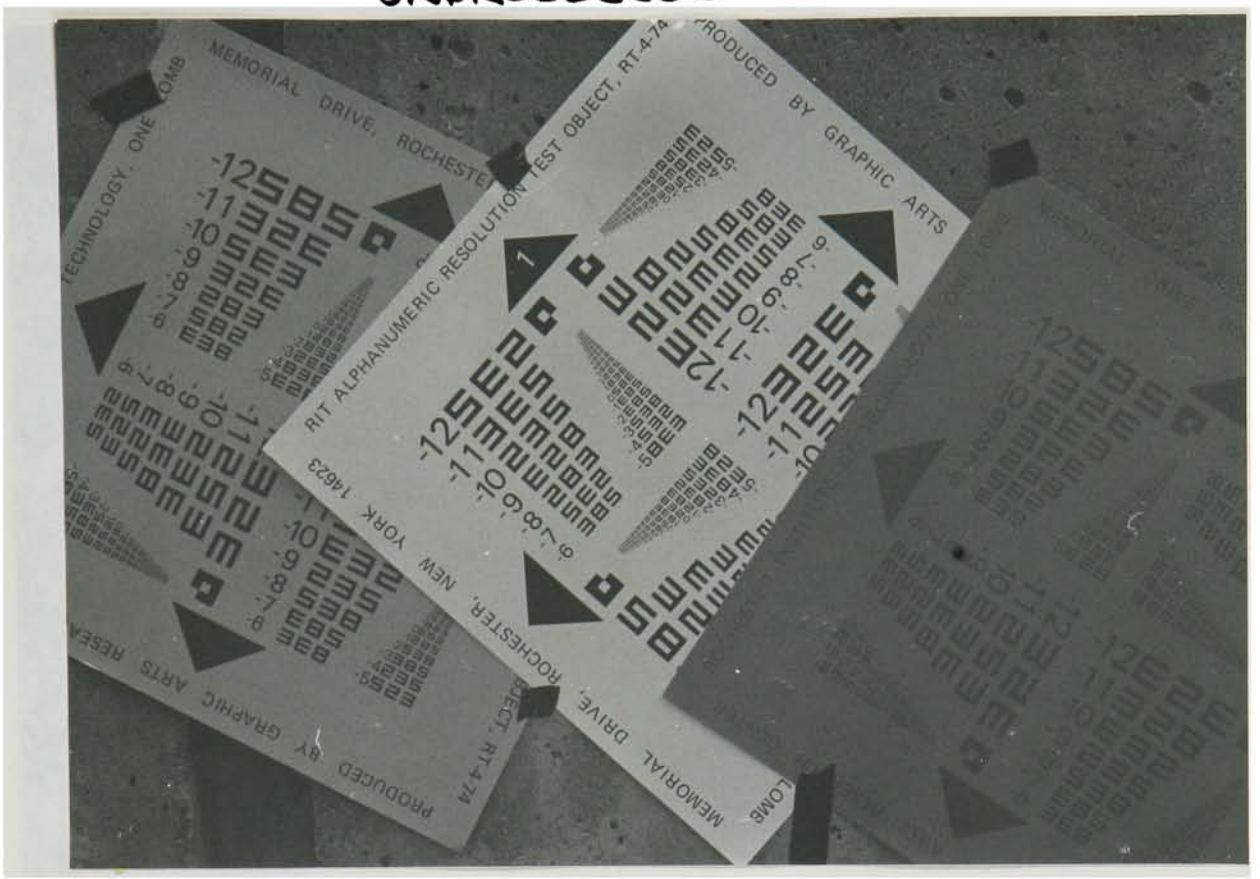


NORMAL

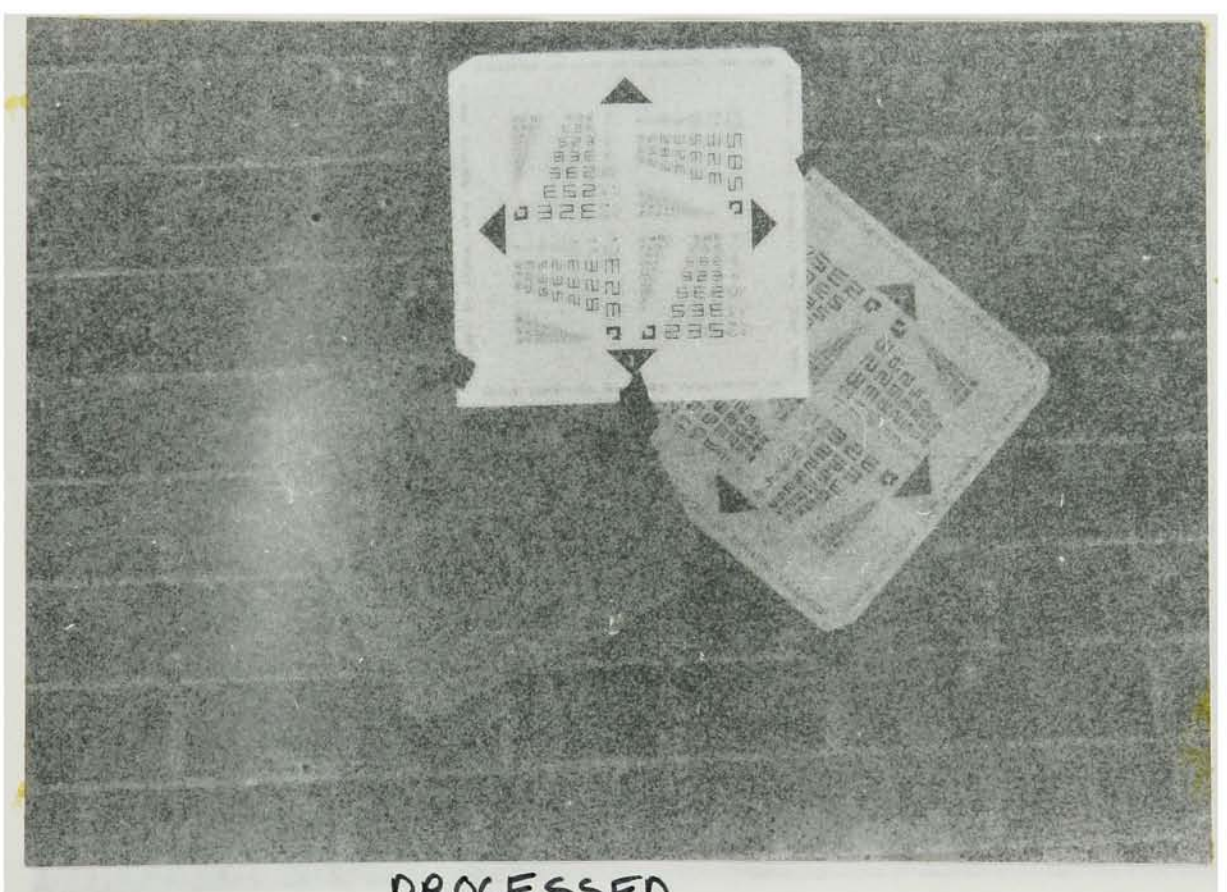


PROCESSED

UNPROCESSED

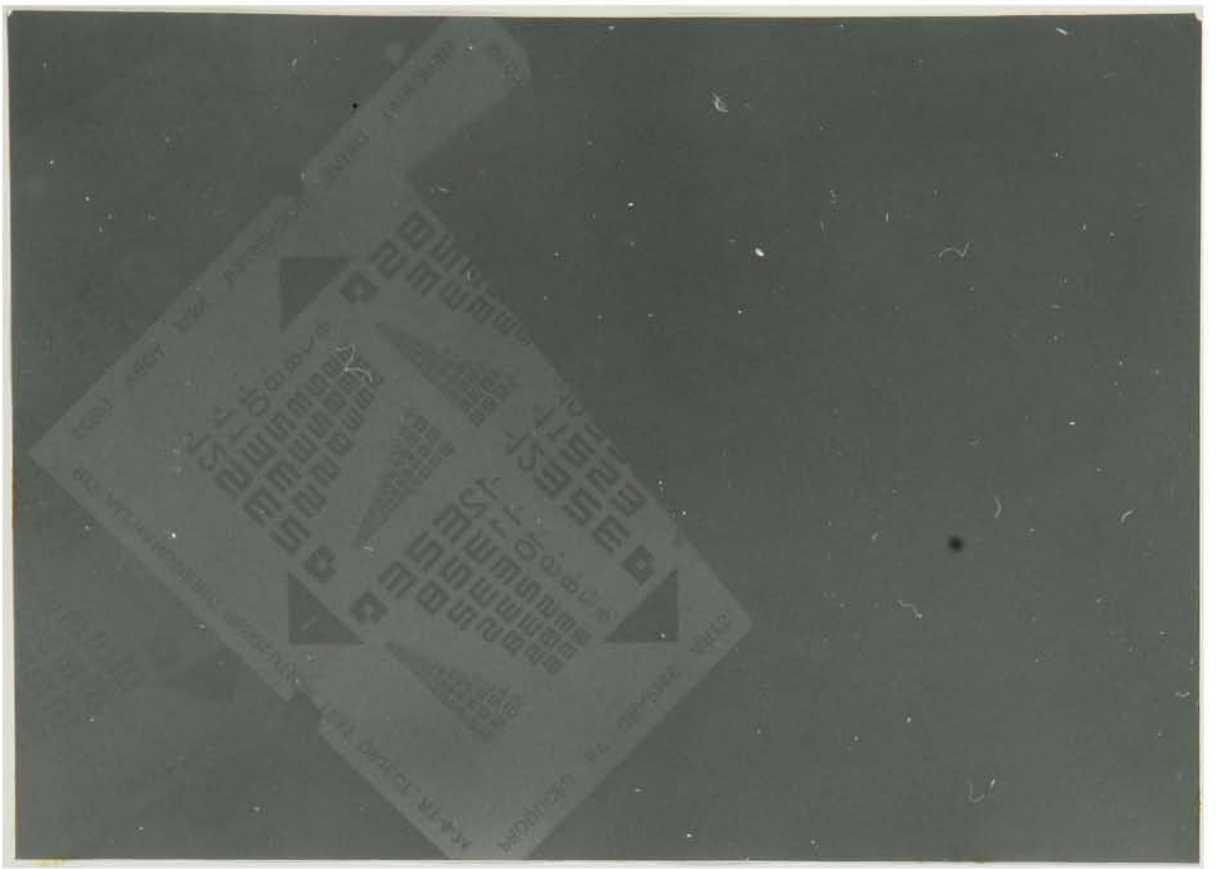


-3 STOPS

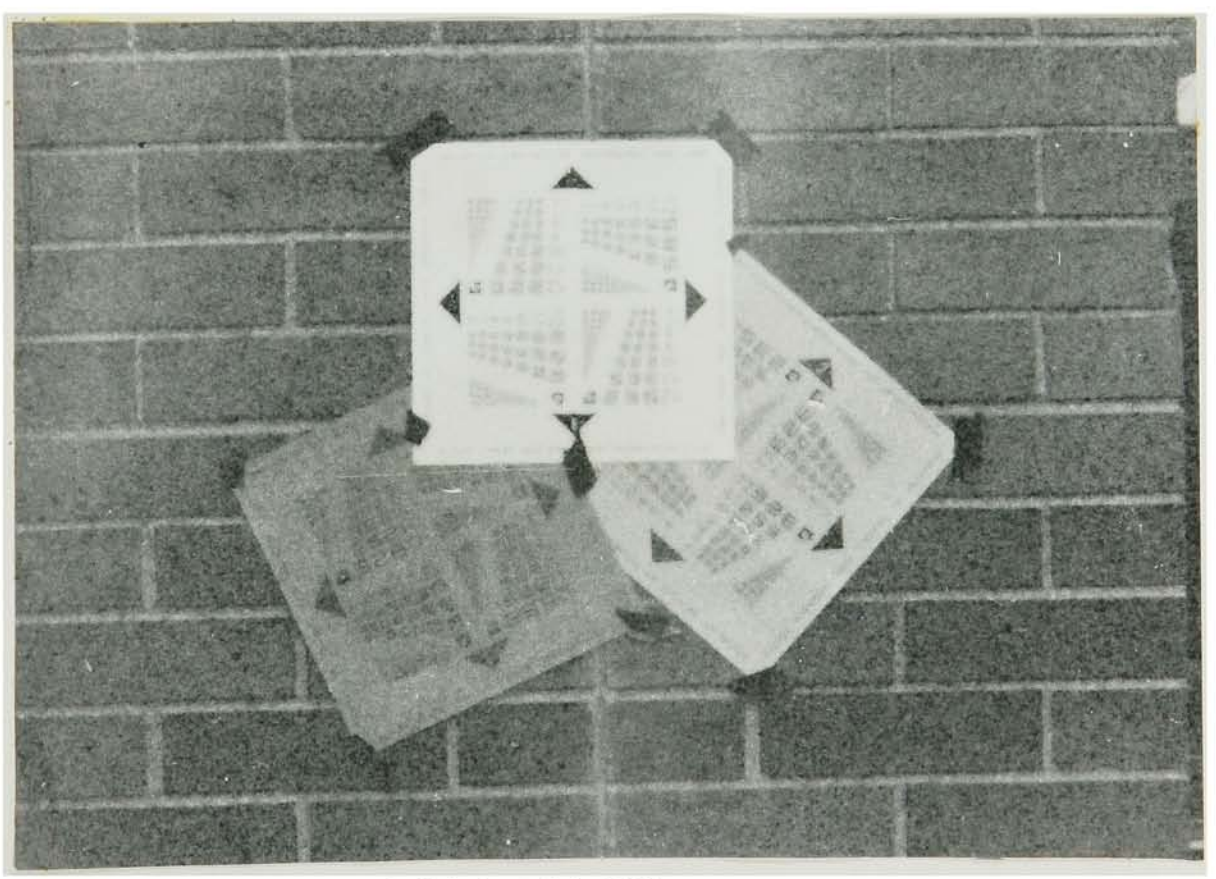


PROCESSED

UNPROCESSED



-5 STOPS



PROCESSED

References

1) US 3,615,491
2) US 3,765,890
3) Thesis for Bachelor of Science, RIT, 1975
4) The Professional Photographer, September 1975, pg. 80
5) Third International Congress on Reprography, London, March 1971, pg. 53
6) Personal communication, Professor Carson
7) Personal communication, Mr. D. Corbin
8) Personal communication, Dr. R. Francis

Bibliography

E. Weyde, Abstracts of P. S. & E., Vol. IX, #5.

E. Ranz, Proceedings of the Third International Congress on Reprography. March 1971, pg. 52

N. T. Notley, P. S. & E., pg. 5, Vol. 11, #1 (1967)

Acknowledgments

The author wishes to thank Agfa-Gevaert, Inc., for its generous donation of Copex Pan film; the Central Intelligence Agency for funding the project; Dr. R. Francis, who served as advisor for the project; and Mr. D. Corbin, for his assistance in the chemistry laboratory.